

EXHIBIT A



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(54) **MULTI-PIECE SOLID GOLF BALL**

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(52) U.S. Cl. **473/357; 524/432**

(58) Field of Search **473/357, 356, 473/359, 372, 374, 371, 373; 524/194, 908, 432, 526, 534**

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,683,257 A * 7/1987 Kakiuchi et al. 473/372
 4,929,678 A * 5/1990 Hamada et al. 525/193
 4,955,613 A * 9/1990 Gendreau et al. 260/998.14
 5,252,652 A * 10/1993 Egashira et al. 473/372

5,733,205 A * 3/1998 Higuchi et al. 473/373
 6,045,460 A * 4/2000 Hayashi et al. 473/376
 6,194,505 B1 * 2/2001 Sone et al. 473/371
 6,315,679 B1 * 11/2001 Sano 473/357

FOREIGN PATENT DOCUMENTS

EP 0 920 886 A2 6/1999
 GB 2 324 740 A 11/1998

OTHER PUBLICATIONS

M. R. Farrally, A. J. Cochran, "Science and Golf III", 1999, Human Kinetics, pp. 410, 412, 413.
 British Search Report, Oct. 17, 2002.

* cited by examiner

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(57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity η of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

9 Claims, No Drawings

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MULTI-PIECE SOLID GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance

2. Prior Art

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio Mw/Mn of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

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soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played

The inventor has discovered that golf balls having a solid core, an inner cover layer over the cover, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C as a 5 wt % solution in toluene of up to 600 mPa s, and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity (ML_{1+1} (100° C)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer

The polybutadiene (a) is typically synthesized using a rare-earth catalyst

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML_{1+1} (100° C)) of not more than 55, and satisfies the relationship $\eta \leq 20A - 550$, wherein A is the Mooney viscosity (ML_{1+1} (100° C)) of the second polybutadiene and η is the viscosity, in mPa s, of the second polybutadiene at 25° C as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60

DETAILED DESCRIPTION OF THE INVENTION

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity η at 25° C as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index Mw/Mn have each been optimized

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least

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90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines.

The polybutadiene (a) must also have a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity η at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity η lowers the workability of the rubber composition. It is recommended that the viscosity η be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity η may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene. A is preferably at least $10B+7$, more preferably at least $10B+8$ and most preferably at least $10B+9$, but preferably not more than $10B+55$, more preferably not more than $10B+50$, and most preferably not more than $10B+45$. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity (ML_{1+4} (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol ML_{1+4} (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

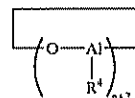
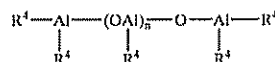
Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula $AlR^1R^2R^3$ (wherein R^1 , R^2 and R^3 are

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each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas, R^4 is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula AlX_nR_{3-n} (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as Me_3SrCl , Me_2SrCl_2 , $MeSrHCl_2$ and $MeSrCl_3$ (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

- (1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas $R^5_nM'X_{4-n}$, $M'X_4$, $M'X_3$, $R^5_nM'(-R^6-COOR^7)_{4-n}$ or $R^5_nM'(-R^6-COR^7)_{4-n}$ (wherein R^5 and R^6 are each independently a hydrocarbon group of 1 to 20 carbons; R^7 is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain; M' is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);
- (2) heterocumulene compounds containing on the molecule a $Y=C=Z$ linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);

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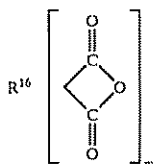
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- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



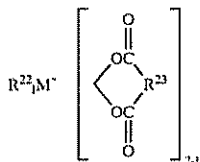
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyanate compounds;
- (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas $R^8-(COOH)_m$, $R^9(COX)_m$, $R^{10}-(COO-R^{11})$, $R^{12}-OCOO-R^{13}$, $R^{14}-(COOCO-R^{15})_m$ or the following formula



(wherein R^8 to R^{16} are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula $R^{17}_1M''(OCOR^{18})_{1-1}$, $R^{19}_1M''(OCO-R^{20}-COOR^{21})_{1-1}$ or the following formula



(wherein R^{17} to R^{23} are each independently a hydrocarbon group of 1 to 20 carbons, M'' is a tin atom, a silicon atom or a germanium atom; and 1 is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %

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In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and η have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a)

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkyl lithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A - 750 \leq \eta \leq 20A - 550$$

wherein η is the viscosity of the second polybutadiene at 25° C as a 5 wt % solution in toluene and A is the Mooney viscosity (ML₁₊₄ (100° C)) of the second polybutadiene

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The viscosity η is preferably at least 20A–700, more preferably at least 20A–680, and most preferably at least 20A–650, but preferably not more than 20A–560, more preferably not more than 20A–580, and most preferably not more than 20A–590. The use of a polybutadiene having such an optimized relationship of η and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyldisulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

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carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Lupercol 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200°C for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate

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rebound that results in a poor carry, and a poor durability to cracking with repeated impact

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.) Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.)

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65

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It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played

EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof

Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone

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TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	η	10B + 5	10B + 60	20A - 550
Polybutadiene									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
Rubber formulation (pbw)									
(1)						50			
(2)	70	30	50		50	50		50	
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
Core formulation (pbw)									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4	0.7	0.7	1.4	1.4	1.4	1.4
1,1-Bis(l-butylperoxy)-3,3,5-trimethylcyclohexane				0.3	0.3				
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of pentachlorothiophenol	1	1	2	1	1	1	0	1	1

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg)

Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surlyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation.

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as "Too hard," "Good" or "Too soft." The rating assigned most often to a particular ball was used as that ball's overall rating.

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TABLE 3

	A	B	C	D	E	F	G
Formulation (pbw)							
Himilan 1706	50	70					
Himilan 1605	50						
Himilan 1557							20
Himilan 1855							30
Himilan AM7316		12					
Surlyn 8945			35				
Surlyn 9945			35				
Surlyn 8120				100			50
Dynatron 6100P			30				
Pandex T8290					50		15
Pandex T8295					50	100	
Behenic acid		16					
Magnesium oxide		2					
Titanium dioxide	4	2	4	4	2.7	2.7	4

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Japanese patent application Ser No 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1 A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C. as a 5 wt % solution in toluene of up to 600 mPa s, being synthesized using a rare-earth catalyst and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity (ML_{1+1} (100° C)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

	Example					Comparative Example				
	1	2	3	4	5	1	2	3	4	
<u>Core properties</u>										
Deflection (mm) under 980 N load	3.8	3.8	3.5	3.5	3.3	3.3	3.5	3.5	3.3	
Specific gravity	1.15	1.15	1.15	1.21	1.21	1.21	1.21	1.21	1.21	
Rebound (m/s)	+0.9	+0.9	+1.1	+0.7	+0.8	+0.3	0	+0.5	+0.5	
<u>Inner cover layer</u>										
Type	A	B	C	A	B	B	A	D	D	
Shore D hardness	63	60	56	63	60	60	63	45	45	
Specific gravity	0.98	0.97	0.97	0.98	0.97	0.97	0.98	0.98	0.98	
Thickness (mm)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	
<u>Outer cover layer</u>										
Type	E	F	F	G	G	G	G	G	A	
Shore D hardness	47	51	51	53	53	53	53	53	63	
Specific gravity	1.18	1.18	1.18	0.98	0.98	0.98	0.98	0.98	0.98	
Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
<u>Golf ball properties</u>										
When hit with No. 1 Wood at HS of 50 m/s										
Carry (m)	227.0	226.9	226.7	226.9	226.7	223.8	222.2	217.7	220.8	
Total distance (m)	258.5	258.8	258.3	258.3	258.0	255.0	253.4	248.3	252.8	
Spin rate (rpm)	3205	3153	3241	3125	3180	3182	3121	3305	3177	
Feel on impact	good	good	good	good	good	good	good	too soft	good	
Spin rate on approach shot (sand wedge; HS 20 m/s)	6323	6251	6226	6118	6111	6107	6113	6186	4308	
Feel of ball	good	good	good	good	good	good	good	too soft	too hard	

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(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,

(d) 0.1 to 5 parts by weight of an organosulfur compound,

(e) 5 to 80 parts by weight of an inorganic filler,

(f) 0.1 to 5 parts by weight of an organic peroxide;

the inner cover layer has a Shore D hardness of 50 to 80;

the outer cover layer has a Shore D hardness of 35 to 60; and

the outer cover layer has a lower Shore D hardness than the inner cover layer.

2 The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML_{1+4} (100° C.)) of not more than 55, and satisfies the relationship:

$$\eta \leq 20A - 550,$$

wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the second polybutadiene and η is the viscosity of the second polybutadiene, in mPa·s, at 25° C as a 5 wt % solution in toluene

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3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst

4 The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity (ML_{1+4} , 100° C.) of 40 to 60.

5 The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units

6 The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units

7 The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units

8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.

9 The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst

* * * * *

EXHIBIT B



US005252652A

United States Patent [19]

Egashira et al.

[11] Patent Number: 5,252,652

[45] Date of Patent: Oct. 12, 1993

[54] **SOLID GOLF BALL**

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[21] Appl. No.: 521,618

[22] Filed: May 10, 1990

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[51] Int. Cl.⁵ C08K 5/09; C08K 5/36;
A63B 37/00

[52] U.S. Cl. 524/392; 524/289;
524/382; 524/908; 273/218

[58] Field of Search 524/908, 289, 382, 392

[56] References Cited

U.S. PATENT DOCUMENTS

2,378,519 6/1945 Vincent 524/392
2,467,789 4/1949 Verbanc et al. 524/382

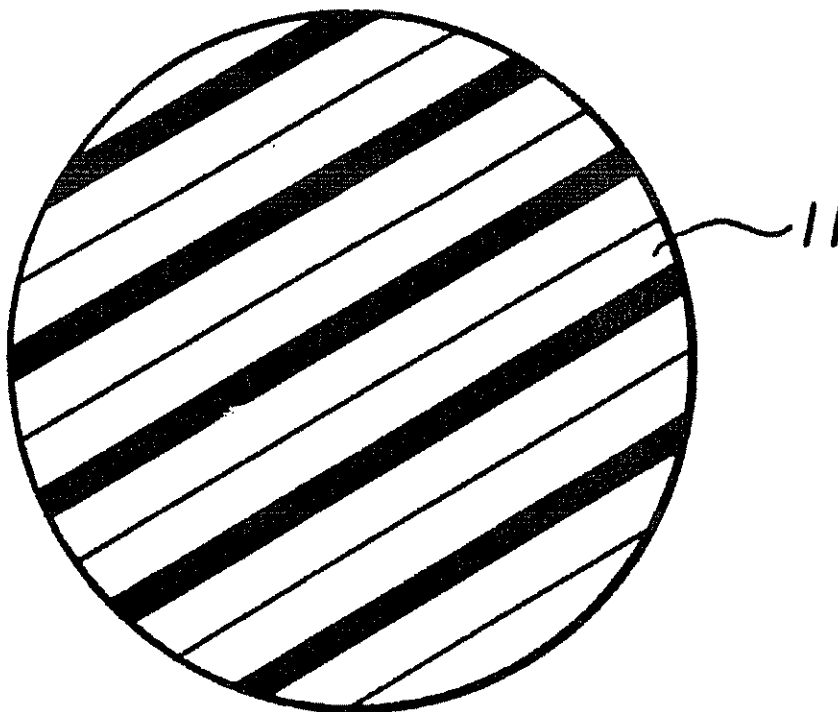
2,543,845 3/1951 Fryling 524/392
3,175,992 3/1965 Anderson, Jr. 524/392
3,804,421 4/1974 Alex et al. 293/218
3,923,719 12/1975 Gattuso 524/392
4,076,255 2/1978 Moore et al. 273/218
4,129,538 12/1978 Kaplan et al. 524/392
4,398,000 8/1983 Kataoka et al. 523/206
4,556,220 12/1985 Tomina et al. 524/908
4,595,721 6/1986 Devaux et al. 524/392
4,683,257 7/1987 Kakiuchi et al. 524/908
4,735,980 4/1988 Sturm et al. 524/392
4,770,422 9/1988 Isaac 524/708

Primary Examiner—Kriellion S. Morgan*Attorney, Agent, or Firm*—Sughrue, Mion, Zinn,
Macpeak & Seas

[57]

ABSTRACT

One-piece and multi-layered golf balls are improved in flying performance by forming the one-piece ball entirely or multi-layered golf ball core from a rubber composition comprising a base rubber, an unsaturated carboxylic acid metal salt, and an organic sulfur compound and/or a metal salt thereof.

13 Claims, 1 Drawing Sheet

U.S. Patent

Oct. 12, 1993

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FIG. 1

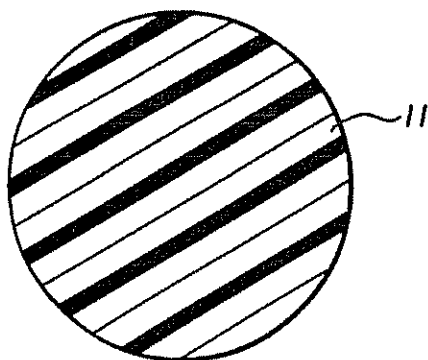
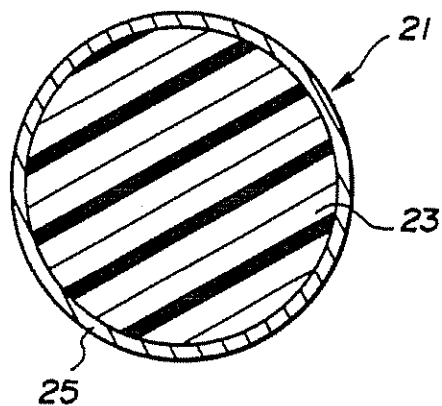


FIG. 2



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SOLID GOLF BALL

This invention relates to solid golf balls having improved flying performance.

BACKGROUND OF THE INVENTION

In general, solid golf balls include a one-piece golf ball which is integrally molded in its entirety a two-piece golf ball having a core enclosed in a cover, and a multi-layered golf ball having a core enclosed in a cover through one or more intermediate layers.

These solid golf balls have an elastic portion in the form of a molded and vulcanized rubber compound as a portion, that is, a core in the case of multi-layered golf balls or as their entirety in the case of one-piece golf balls. For the purpose of improving the repulsion coefficient and impact resistance of the prior art rubber compositions from which the elastic portion was formed, attempts were made to blend a monomer having an unsaturated bond, typically an α,β -ethylenically unsaturated carboxylic acid metal salt as a co-crosslinking agent in polybutadiene or a similar base rubber. The co-crosslinking agent will graft or crosslink to the backbone of polybutadiene rubber under the action of a peroxide or similar co crosslinking initiator, resulting in a three-dimensional crosslinked polymer, which can provide an adequate degree of hardness and durability for one-piece golf balls or multi-layered golf ball cores. Therefore, one-piece golf balls formed from rubber compositions having such a co-crosslinking agent blended and multi-layered golf balls having cores formed from rubber compositions having such a co-crosslinking agent blended are known to exhibit satisfactory flying performance and durability.

Golf players have a continuous demand for better flying performance and it is thus desired to develop golf balls having further improved flying performance.

SUMMARY OF THE INVENTION

Therefore, an object of the invention is to provide a golf ball having further improved flying performance.

Searching for an optimum additive for a rubber composition containing a base rubber, typically polybutadiene and an unsaturated carboxylic acid metal salt as a co-crosslinking agent, the inventors have found that when an organic sulfur compound and/or a metal-containing organic sulfur compound is added to the rubber composition, there is obtained a rubber composition which can be vulcanized into a rubbery elastomer having improved rebound resilience. If a one piece golf ball or a multi-layered golf ball core is formed from this rubber composition, the resulting solid golf ball exhibits an increased initial velocity upon hitting and improved flying performance. The present invention is predicated on this finding.

According to the present invention, there is provided a solid golf ball comprising a rubber composition containing a base rubber, an unsaturated carboxylic acid metal salt, and a sulfur compound selected from the group consisting of an organic sulfur compound and a metal-containing organic sulfur compound.

In one form, the ball is a one-piece golf ball which is entirely formed of the present rubber composition.

In another form, the ball is a multi-layered golf ball comprising a core and a cover enclosing the core, wherein the core is formed of the present rubber com-

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position. The core may be enclosed in the cover directly or through an intermediate layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross section of a one-piece golf ball.

FIG. 2 is a cross section of a two-piece golf ball

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows in cross section a one-piece golf ball 11. FIG. 2 shows a two-piece golf ball 21 comprising a core 23 coated with a cover 25. A plurality of, usually 200 to 600, dimples are formed on the surface of the golf balls, although they are not shown in FIGS. 1 and 2.

The solid golf ball of the present invention is a one piece golf ball or a multi-layered golf ball in which the one-piece golf ball or the core of the multi-layered golf ball is formed from a rubber composition comprising a base rubber, an unsaturated carboxylic acid metal salt, and an organic sulfur compound and/or a metal-containing organic sulfur compound.

The base rubber used herein may be any desired rubber which is commonly used in conventional one-piece golf balls and cores of multi-layered golf balls. Polybutadiene rubbers, especially poly(1,4-butadiene) rubbers containing at least 40 mol %, preferably 80 to 100 mol % of cis-1,4 bond are preferred because of high rebound resilience, extrusion moldability, and high strength after vulcanization. If desired, the poly(1,4-butadiene) rubbers may be blended with natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like. It is desired that at least 80% by weight of poly(1,4-butadiene) rubber be present in the base rubber because base rubbers containing less amounts of poly(1,4-butadiene) rubber often fail to take advantage of the rebound resilience of polybutadiene rubber.

The metal salt of unsaturated carboxylic acid is blended as a co-crosslinking agent. Examples include zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid, methacrylic acid, maleic acid, and fumaric acid, with the zinc salts of acrylic and methacrylic acid being most preferred. The unsaturated carboxylic acid metal salt may be blended in a rubber either as a preformed metal salt or by introducing an α,β -unsaturated carboxylic acid and a metal oxide or hydroxide into the rubber composition and allowing them to react in the rubber composition to form a metal salt. The unsaturated carboxylic acid metal salt may be blended in any desired amount, but preferably in amounts of about 25 to about 40 parts by weight per 100 parts by weight of the base rubber.

The rubber composition used in the manufacture of the solid golf ball of the invention contains an organic sulfur compound and/or a metal-containing organic sulfur compound in addition to the base rubber and the unsaturated carboxylic acid metal salt. Examples of the organic sulfur compound include thiophenols such as pentachlorothiophenol, 4-butyl-o-thiocresol, 4 t-butyl-p-thiocresol, and 2-benzamidothiophenol, thiocarboxylic acids such as thio-benzoic acid, and sulfides such as dixylyl disulfide, di(o-benzamidophenyl) disulfide and alkylated phenol sulfides. Examples of the metal-containing organic sulfur compound include zinc salts of the above-mentioned thiophenols and thiocarboxylic acids. The sulfur compounds may be used alone or in admixture of two or more of them. The sulfur compound is preferably blended in amounts of from about 0.05 to about 2 parts by weight, more preferably from

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about 0.1 to about 0.5 parts by weight per 100 parts by weight of the base rubber.

The rubber composition of the invention may further contain a co-crosslinking initiator. Preferred examples of the co-crosslinking initiator include organic peroxides, such as dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl-cyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2-bis(t-butylperoxy-isopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene, with the dicumyl peroxide being most preferred. The initiator may be blended in amounts of about 0.5 to about 3 parts by weight, preferably about 1 to about 2.5 parts by weight per 100 parts by weight of the base rubber.

Also employable is a filler. Preferred examples of the filler include metal oxides such as zinc oxide and magnesium oxide. It may be blended in amounts of about 10 to about 80 parts by weight per 100 parts by weight of the base rubber. If desired, the rubber composition can additionally contain a plasticizer, an antioxidant, and any other additives which are generally employed in the preparation of one-piece balls or cores of multi-layered balls. Their amounts may be determined without undue experimentation.

The solid golf ball of the invention may be prepared by molding the above-formulated rubber composition as formulated above into a desired spherical shape, that is, a ball in the case of a one-piece ball or into a core in the case of a multi-layered ball and vulcanizing the rubber by heating. The manufacture may be in accord with conventional method and conditions.

When multi-layered golf balls such as two-piece balls are manufactured, the core is coated with a cover. The cover material used herein may be selected from commonly used cover materials, for example, ionomers such as Surllyn®, polyesters, and nylons. The cover usually has a thickness of 0.5 to 2.5 mm.

The core may be enclosed in the cover directly or through an intermediate layer.

The present invention may be applied to any type of golf ball including small balls having a diameter of at least 41.15 mm and a weight of up to 45.92 g, and large balls having a diameter of at least 42.67 mm and a weight of up to 45.92 g.

The distribution and total number of dimples are not critical although 300 to 550 dimples, preferably 350 to 540 dimples are generally formed on a ball. Preferred dimple arrangements are regular icosahedral, regular dodecahedral, and regular octahedral arrangements. The dimples is preferably distributed uniformly on the ball surface in such an arrangement.

The solid golf balls of the invention are of the above-mentioned construction and exhibit excellent flying performance.

EXAMPLE

Examples of the invention are given below together with comparative examples by way of illustration and not by way of limitation.

EXAMPLES 1-6

Solid cores for two-piece golf balls were prepared and compared with conventional two-piece golf ball cores.

Six rubber compositions were prepared by mixing the ingredients shown in Table 1. A two-piece golf ball-forming solid core having a diameter of 38.0 mm was prepared by molding each of the compositions in a mold

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followed by vulcanization at 155° C for 20 minutes. The cores were examined by a hitting test according to the USGA standard. Using a hitting machine of the flywheel type, the cores were hit at a head speed of 38 m/sec. to measure the initial velocity (in m/sec.) The results are shown in Table 1.

TABLE 1

	Core No.					
	1	2	3	4*	5*	6*
<u>Ingredients (pbw)</u>						
Poly(cis-1,4-butadiene)	100	90	80	100	90	80
Poly(cis-isoprene)	0	10	20	0	10	20
Zinc acrylate	32	32	32	32	32	32
Zinc oxide	21	21	21	21	21	21
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	1.5	1.5	1.5	1.5	1.5	1.5
Pentachlorothiophenol	0.2	0.2	0.2	0	0	0
zinc salt						
Initial velocity, m/sec.	73.32	73.11	72.80	72.95	72.67	72.30

*outside the scope of the invention

As seen from Table 1, the performance, that is, initial velocity upon hitting of the core is improved by blending zinc salt of pentachlorothiophenol which is a metal salt of an organic sulfur compound in a rubber composition.

Examples 7 and 8

Two rubber compositions were prepared by blending the ingredients shown in Table 2. Two-piece golf ball solid cores having a diameter of 38 mm were prepared by molding the composition in a mold and vulcanizing at 155° C. for 20 minutes. An ionomer resin composition was applied to the cores to form a cover thereon. There were obtained two-piece golf balls having a diameter of 42.7 mm.

The balls were measured for weight, hardness and initial velocity. The hardness of the balls was measured as a deflection (in mm) under a load of 100 kg. The initial velocity (in m/sec.) of the balls was measured by a hitting test according to the USGA standard in which the balls were hit at a head speed of 38 m/sec. using a hitting machine of the flywheel type. The results are shown in Table 2.

TABLE 2

	Example	
	7	8*
<u>Core composition (pbw)</u>		
Poly(cis-1,4-butadiene) rubber	100	100
Zinc acrylate	32	32
Zinc oxide	21	21
Antioxidant	0.2	0.2
Dicumyl peroxide	1.5	1.5
Pentachlorothiophenol zinc salt	0.2	—
<u>Ball properties</u>		
Weight, g	45.3	45.3
Hardness	2.30	2.32
Initial velocity, m/sec.	73.37	72.84

*outside the scope of the invention

As seen from Table 1, the golf balls of the invention are improved in initial velocity upon hitting and hence, in flying performance.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the

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appended claims, the invention may be practices otherwise than as specifically described.

We claim:

1. A solid golf ball, having an improved rebound property and initial velocity, comprising a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber, about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms, about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2-benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and about 0.5 to about 3 parts by weight of an organic peroxide.

2. The solid golf ball of claim 1, wherein said solid golf ball is a one-piece golf ball which is formed of said rubber composition

3. The solid gold ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition

4. The solid golf ball of claim 3, wherein said solid golf ball is a two-piece ball, and said core is directly enclosed in the cover.

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5. The solid gold ball of claim 3, wherein said solid golf ball further comprises an intermediate layer between the core and the cover.

6. The solid golf ball of claim 1, wherein said base rubber is a polybutadiene rubber.

7. The solid gold ball of claim 6, wherein said polybutadiene rubber is a poly(1,4-butadiene) rubber containing at least 40 mol % of cis-1,4 bond.

8. The solid golf ball of claim 7, wherein said poly(1,4-butadiene) rubber contains at least 80 to 100 mol % of cis-1,4 bond.

9. The solid golf ball of claim 7, wherein said base rubber comprises at least 80% by weight of said poly(1,4-butadiene) rubber.

10. The solid golf ball of claim 9, wherein said poly(1,4-butadiene) rubber is blended with a natural rubber, a polyisoprene rubber of a styrene-butadiene rubber.

11. The solid gold ball of claim 1, wherein said sulfur compound is blended in an amount of from about 0.1 to about 0.5 parts by weight.

12. The solid golf ball of claim 1, wherein said organic peroxide is selected from the group consisting of dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2'-bis(t-butylperoxyisopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene.

13. The solid golf ball of claim 1, wherein said rubber composition further comprises a filler.

* * * * *

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EXHIBIT C



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(12) **United States Patent**
Watanabe

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(45) **Date of Patent:** **Jan. 20, 2004**

(54) **GOLF BALL**

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(73) **Assignee:** **Bridgestone Sports Co., Ltd., Tokyo (JP)**

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(52) **U.S. Cl.** **473/371; 473/351**

(58) **Field of Search** **473/251-377**

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,002,281 A * 3/1991 Nakahara et al. 473/373
5,072,944 A * 12/1991 Nakahara et al. 473/373
5,184,828 A 2/1993 Kim et al.
5,645,496 A 7/1997 Endo et al.
5,711,723 A 1/1998 Hiraoka et al.
5,782,707 A * 7/1998 Yamagishi et al. 473/374
5,803,833 A * 9/1998 Nakamura et al. 473/377
5,830,085 A * 11/1998 Higuchi et al. 473/373
6,190,269 B1 * 2/2001 Moriyama 473/373
6,287,218 B1 * 9/2001 Ohama 473/377
6,315,682 B1 * 11/2001 Iwami et al. 473/370

6,319,155 B1 * 11/2001 Moriyama et al. 473/371
6,336,872 B1 * 1/2002 Moriyama et al. 473/374
6,354,967 B1 * 3/2002 Nakamura et al. 473/377
6,358,159 B1 * 3/2002 Yamagishi et al. 473/374
6,379,268 B1 * 4/2002 Yamagishi et al. 473/371

FOREIGN PATENT DOCUMENTS

JP 10-127823 5/1998
JP 11-290479 10/1999
JP 11-333026 12/1999

OTHER PUBLICATIONS

Farrally, M.R. et al, Science and Golf III: Proceedings of the 1998 World Scientific Congress of Golf, Illinois: Human Kinetics, copyright 1999, p 413 *

* cited by examiner

Primary Examiner—Paul I. Sewell

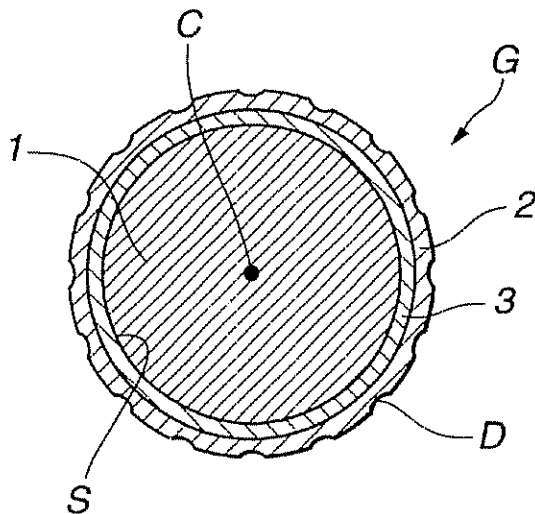
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(57) **ABSTRACT**

A multi-piece golf ball includes a rubbery elastic core, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof. The center and surface of the elastic core have a hardness difference of at least 18 JIS-C hardness units. This construction and combination of features improve the distance of the ball when struck with a driver, provide the ball with excellent spin characteristics and thus good controllability on approach shots, and gives the ball a good feel on impact, enabling the ball to meet the high expectations of skilled golfers.

27 Claims, 1 Drawing Sheet

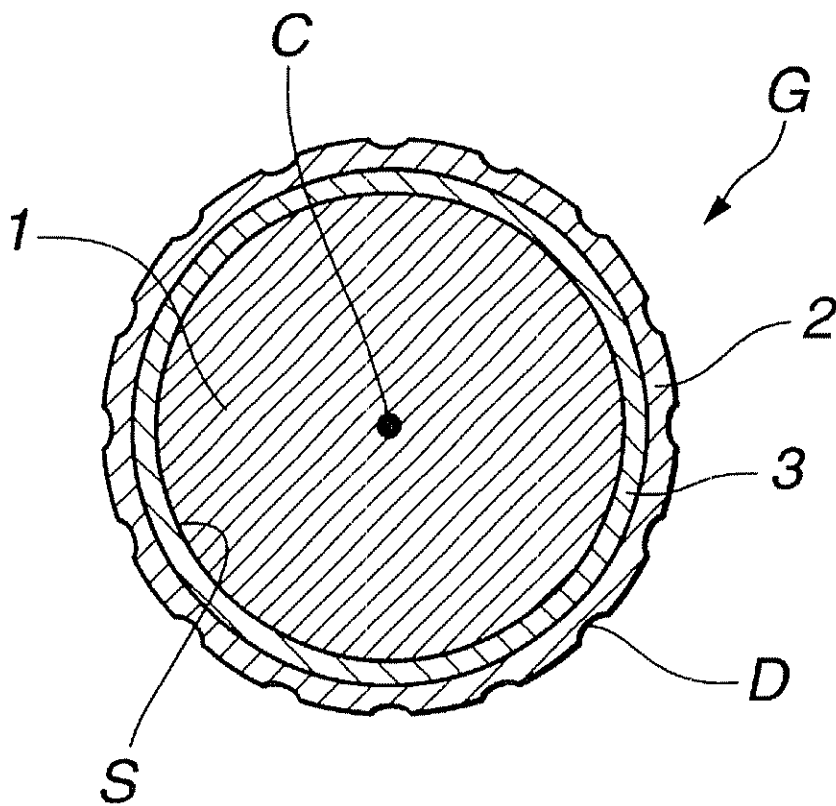


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FIG.1



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GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a golf ball having a multilayer construction of at least three layers which includes a core, an intermediate layer and a cover. More particularly, the invention relates to a golf ball which has good rebound characteristics and provides an excellent travel distance, controllability and "feel" upon impact with a golf club.

2. Prior Art

In recent years, solid golf balls, with their good flight performance, have consistently won greater general approval than conventional thread-wound golf balls.

Solid golf ball constructions include two-piece balls made of a solid, high-resilience, rubber core enclosed within a relatively thin resin cover, and multi-piece balls having a core, a cover, and also an intermediate layer therebetween whose properties differ somewhat from those of the cover.

As already noted, because of their good flight performance (i.e., long travel distance), solid golf balls of these types are widely favored by both amateur and professional golfers. Yet, there remains a desire among golfers for even better flight performance.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a golf ball having a multilayer construction of three or more layers that is endowed with improved distance without diminishing the controllability and feel that are so important to skilled golfers.

Accordingly, the invention provides a golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 18 between the center and the surface.

Preferably, the JIS-C hardness at the center of the core is 50 to 65, and the JIS-C hardness at the surface of the core is 70 to 90. The core typically undergoes a deformation of 3.0 to 5.0 mm when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

BRIEF DESCRIPTION OF THE DRAWING

The objects, features and advantages of the invention will become more apparent from the following detailed description, taken in conjunction with the accompanying diagram.

The only FIGURE, FIG. 1 is a sectional view showing a golf ball according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, the golf ball G of the present invention has a construction composed of at least three layers, commonly known as a "multi-piece construction," which include a rubbery elastic core 1, a cover 2 that is

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generally made of a resin material and has a plurality of dimples D on the surface thereof, and one or more intermediate layer 3 between the core 1 and the cover 2, all situated in a concentric fashion. The illustrated embodiment has a single intermediate layer. The intermediate layer 3 is made of a resin material which is harder than the cover 2. The core 1 having a center C and a surface S at its radially outer extremity has a JIS-C hardness which gradually increases radially outward from the center C to the surface S. The core 1 is formed so as to have a specific hardness difference between the surface S and the center C.

The inventive golf ball includes a hard intermediate layer disposed between the core, which has an optimized hardness profile, and the cover which is softer than the intermediate layer. This construction provides the ball with an excellent "feel," holds down spin when the ball is struck with a driver, and increases the distance traveled, in part by creating a trajectory which does not describe a high arc when traveling into a headwind. At the same time, it increases the amount of spin on approach shots taken with a club having a large loft angle, thus imparting the excellent control desired in particular by professionals and other skilled golfers.

In the golf ball of the present invention, the core may be made from a known core material which is prepared by blending, for example, a base rubber, the metal salt of an unsaturated carboxylic acid, and an organic peroxide.

The base rubber is preferably polybutadiene. The use of 1,4-polybutadiene, and especially one having a cis structure of at least 40%, is recommended. In addition to the polybutadiene, the base rubber may also include other rubbers such as natural rubber, polyisoprene rubber and styrene-butadiene rubber, if necessary.

Examples of suitable metal salts of unsaturated carboxylic acids include zinc dimethacrylate and zinc diacrylate. Zinc diacrylate is especially preferred for achieving a high rebound energy. It is advantageous to include such unsaturated carboxylic acids in an amount of at least 15 parts by weight, and preferably at least 20 parts by weight, but not more than 50 parts by weight, and preferably not more than 45 parts by weight, per 100 parts by weight of the base rubber.

Examples of suitable organic peroxides include 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di(t-butylperoxy)-m-diisopropylbenzene and 2,5-dimethyl-2,5-di-t-butylperoxyhexane. It is advantageous to include such peroxides in an amount of at least 0.1 part by weight, and preferably at least 0.5 part by weight, but not more than 5 parts by weight, and preferably not more than 2 parts by weight, per 100 parts by weight of the base rubber.

To impart good rebound characteristics, it is advisable to include a suitable compounding ingredient such as a thiophenol, thionaphthol, halogenated thiophenol or metal salt thereof in the core material. Specific examples of such compounding ingredients that may be used include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol. The zinc salt of pentachlorothiophenol is especially preferred. Such a compounding ingredient is typically included in an amount of at least 0.4 part by weight, and preferably at least 0.6 part by weight, but not more than 2.0 parts by weight, and preferably not more than 1.2 parts by weight, per 100 parts by weight of the base rubber. Too much of this ingredient tends to lower the core hardness, which can adversely impact the feel of the ball when hit as well as its durability (cracking resistance), whereas too little may lower the rebound energy of the core, making it impossible for the ball to achieve a sufficient carry.

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If necessary, the core material may include also various additives such as inorganic fillers and antioxidants. Illustrative examples of such additives include zinc oxide, barium sulfate and calcium carbonate.

The core may be fabricated from the above core material by using a conventional process to blend the various ingredients and mold the resulting mixture. For example, the constituent ingredients may be blended in a suitable apparatus such as a Banbury mixer or a kneader to form a "slug," which is then placed in a mold where it is vulcanized at a temperature of generally at least 150° C., and preferably at least 160° C., but generally not more than 190° C., and preferably not more than 180° C. The period of vulcanization is generally at least 8 minutes, and preferably at least 12 minutes, but generally not more than 20 minutes, and preferably not more than 16 minutes.

The weight and diameter of the core may be suitably adjusted according to such factors as the constituent materials and thickness of the intermediate layer and the cover, which are described subsequently. It is recommended that the core generally have a weight of at least 23 g, and preferably at least 30 g, but not more than 37 g, and preferably not more than 35 g. It is also recommended that the core generally have a diameter of at least 33 mm, and preferably at least 36 mm, but not more than 39 mm, and preferably not more than 38 mm.

It is critical for the core to have an optimized hardness profile in which the hardness gradually increases radially outward from the center toward the outside edge or surface of the core. That is, the core has a higher hardness at the surface than at the center.

The core center and surface must have a difference between their respective measured JIS-C hardnesses of at least 18, preferably at least 20, and most preferably at least 22 units. This difference in hardness within the core gives the ball a low spin when hit with a driver (number 1 wood), enabling it to travel well and thus attain a good total distance. Too small a difference in JIS-C hardness between the relatively soft center and the relatively hard surface of the core allows the ball to take on too much spin when hit with a driver, so that it does not travel well and has a short run after it lands on the ground. This makes it impossible to achieve the desired distance. It is recommended that the upper limit in the hardness difference be at most 30, preferably 27 or less, and most preferably 25 units or less.

Specifically, the core at the center typically has a JIS-C hardness of at least 50, and preferably at least 55, but not more than 65, and preferably not more than 62. The core at the surface typically has a JIS-C hardness of at least 70, and preferably at least 75, but not more than 90, and preferably not more than 85. Too low a JIS-C hardness at the core center may deaden the feel and fail to achieve the desired rebound energy, whereas a hardness that is too high may result in an excessively hard feel when the ball is hit. Similarly, too low a JIS-C hardness at the core surface may deaden the feel of the ball when hit, while too high a hardness may result in too hard a feel.

Preferably the core of the inventive golf ball has a deformation of at least 3.0 mm, and preferably at least 3.3 mm, but not more than 5.0 mm, and preferably not more than 4.5 mm, when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf). Too small a deformation may increase the spin when the ball is hit with a driver, preventing the desired travel from being achieved, and may also give the ball too hard a feel. On the other hand, too much deformation may deaden the feel and fail to achieve the necessary rebound energy.

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Since the core has a hardness gradually increasing radially outward from the center to the surface thereof and an optimized difference in hardness between the center and the surface where the core is hardest, the inventive golf ball having the above-described core functions to suppress the generation of excessive spin when it is hit with a driver, effectively increasing the run after it lands on the ground, and thus travelling a longer total distance.

The intermediate layer 3 of the inventive golf ball is an essential layer which is situated between the core 1 and the cover 2 of the ball G, as shown in FIG. 1, and is made of a resin material that is harder than the cover material. Even if the core and cover are within the scope of the present invention, a golf ball lacking the adequate intermediate layer prescribed by the present invention fails to attained the objects of the invention since it cannot adequately suppress spin when hit with a driver, making it impossible to achieve a longer travel distance, and gives a poor feel when hit.

The intermediate layer may be made using a known cover material, illustrative examples of which include an ionomer resin, either by itself or in admixture with a polyester, polyurethane, polyamide, polyolefin or polystyrene thermoplastic elastomer. The use of an ionomer resin by itself is especially preferred, although another thermoplastic resin may be used provided the resin material for the intermediate layer has a greater hardness than the cover. As with the cover material described below, pigments and various other additives may be included in the intermediate material.

The intermediate layer can be formed over the surface of the core using a known process, preferably an injection molding process. For example, once the core is placed within a mold, the intermediate layer material is injection molded over the core in a conventional manner.

The intermediate layer must have a greater hardness than the cover, which is described below. If the intermediate layer has a hardness which is the same as or lower than that of the cover, spin is not adequately suppressed when the ball is hit with a driver, in addition to which the ball has a lower rebound energy, preventing the anticipated total distance from being achieved. It is generally advantageous for the intermediate layer and the cover to have a Shore D hardness difference of at least 2, and preferably at least 5 units, but not more than 20, and preferably not more than 15 units.

It is recommended that the intermediate layer itself have a Shore D hardness of generally at least 50, and preferably at least 55, but not more than 67, and preferably not more than 65.

As already noted, the intermediate layer situated between the core and the cover in the golf ball of the invention has a greater hardness than the cover. The hardnesses of the intermediate layer and the core, when compared using the same hardness scale (i.e., JIS-C hardness or Shore D hardness), are preferably such that the intermediate layer has a greater hardness than the surface of the core. The JIS-C hardness difference between the intermediate layer and the core surface is preferably at least 2, and more preferably at least 6 units, but not more than 22, and more preferably not more than 18 units.

It is recommended that the intermediate layer have a thickness which is generally at least 0.5 mm, but not more than 3 mm, and especially not more than 2 mm. In cases where there are two or more intermediate layers, it is advisable to set the overall thickness of the intermediate layers within the above range.

If the golf ball has two or more intermediate layers situated between the core and the cover, the above-described

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hardness relationship must be maintained between the cover and the outer intermediate layer which is in close contact with the cover

The cover of the golf ball is formed of a material which is softer than the intermediate layer material. Examples of suitable cover materials include ionomer resins and polyurethane thermoplastic elastomers which are softer than the intermediate layer material. The use of an ionomer resin is especially preferred.

It is advantageous for the cover to have a Shore D hardness of generally at least 45, and especially at least 48, but not more than 60, and especially not more than 58. A hardness value that is too low may result in increased spin and an inability to achieve the required total distance. On the other hand, a hardness value that is too high may adversely impact the controllability of shots taken with an iron club having a large loft angle, and approach shots.

A conventional process may be used to form the cover. It is especially preferable to use an injection molding process in which a solid core over which an intermediate layer has been formed is placed within a mold, and the cover material is injection molded over the intermediate layer.

It is recommended that the cover generally have a thickness of at least 0.6 mm, and preferably at least 1.0 mm, but not more than 2.1 mm, and preferably not more than 1.8 mm. Too thin a cover may lower the durability of the ball, whereas a cover that is too thick may lower the ball's rebound energy.

Since the golf ball of the invention has an optimized balance in hardness among the various layers as described above, the ball is endowed with an excellent rebound energy, distance performance, feel, controllability and spin characteristics.

For competition play, the golf ball of the invention may be formed so as to have a diameter and weight which conform with the Rules of Golf. That is, the ball may have a diameter of not less than 42.67 mm and a weight of not greater than 45.93 g.

The inventive golf ball provides increased distance when hit with a driver. On approach shots, the ball has excellent spin characteristics to ensure control as desired. Moreover, it has a good feel on impact. This combination of qualities enables the ball to satisfy the high expectations of skilled golfers in particular.

EXAMPLES

Examples of the invention and comparative examples are given below by way of illustration, and are not intended to limit the invention.

Examples 1-3 and Comparative Examples 1-5

To ascertain the flight characteristics and feel of golf balls according to one embodiment of the invention, golf balls

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with different hardnesses at the center and surface of the core were produced in Examples 1, 2 and 3. A number of additional examples were carried out for the purpose of comparison. The golf balls produced in Comparative Example 1 had cores with a small or flat hardness profile. The balls produced in Comparative Example 2 had cores with a noticeable, yet gradual, hardness profile. The balls produced in Comparative Example 3 had a core with a distinct hardness profile, but had an intermediate layer that was softer than the cover. The balls produced in Comparative Examples 4 and 5 similarly had cores with distinct hardness profiles, but lacked an intermediate layer. Comparative tests were conducted on these various balls.

The balls were all given the same arrangement of dimples on the surface of the cover. Namely, each ball had a total of 432 dimples of three types formed on the cover in an icosahedral arrangement.

Tables 1 and 2 below show the characteristics of the cover and intermediate layer in the ball samples in each example. Table 3 gives the characteristics of the core in the same balls, and Table 4 presents the test results obtained for each type of ball.

TABLE 1

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Cover	Material	a	a	a	a	a	b	a	a
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Hardness (Shore D)	55	55	55	55	55	65	55	55
Intermediate layer	Material	b	b	b	b	b	a	—	—
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	—	—
	Hardness (Shore D)	65	65	65	65	65	55	—	—

TABLE 2

Cover, intermediate layer		a	b
Composition (parts by weight)	Himilan AM7317 (Zn) ¹⁾		50
	Himilan 1650 (Zn) ²⁾	50	
	Himilan AM7318 (Na) ³⁾		50
	Surlyn 8120 (Na) ⁴⁾	50	
Hardness	Titanium oxide	5	5
	Shore D hardness	55	65
	JIS-C hardness	80	94

¹⁾A zinc ionomer resin having an acid content of 18% made by DuPont-Mitsui Polychemicals Co., Ltd.

²⁾A zinc ionomer resin made by DuPont-Mitsui Polychemicals Co., Ltd.

³⁾A sodium ionomer resin having an acid content of 18% made by DuPont-Mitsui Polychemicals Co., Ltd.

⁴⁾A sodium ionomer resin made by E. I. DuPont de Nemours and Co.

TABLE 3

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Core	Composition (pbw)	100	100	100	100	100	100	100	100
	1,4-cis-Polybutadiene	41.0	38.0	35.0	28.0	27.8	38.0	32.1	28.4
	Zinc diacrylate	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Peroxide (1) ¹⁾	0.8	0.8	0.8	0.6	0.6	0.8	0.8	0.8
	Peroxide (2) ²⁾	0.1	0.1	0.1	0	0	0.1	0.1	0.1
	Sulfur ³⁾	0	0	0	0.2	0.2	0	0	0
	Antioxidant ⁴⁾	24.1	25.2	26.4	29.8	29.9	25.2	12.8	14.4
	Barium sulfate	5	5	5	5	5	5	5	5
	Zinc oxide								

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TABLE 3-continued

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Vulcanization conditions	Zinc salt of pentachlorothiophenol	1	1	1	0.2	0.2	1	1	1
	Primary Temperature (°C)	175	175	175	140	155	175	175	175
	Time (min)	15	15	15	30	15	15	15	15
	Secondary Temperature (°C)	—	—	—	165	—	—	—	—
	Time (min)	—	—	—	15	—	—	—	—
Hardness	Surface (JIS-C hardness)	85	83	78	76	76	83	87	80
	Center (JIS-C hardness)	61	59	55	72	60	59	63	56
	JIS-C hardness difference	24	24	23	4	16	24	24	24
Deformation under loading (mm) ⁵⁾		3.4	3.8	4.1	3.3	3.4	3.8	3.4	4.1

¹⁾Dicumyl peroxide, produced by NOF Corporation under the trade name Percumyl D.²⁾1,1-Bis(1-butylperoxy)-3,3,5-trimethylcyclohexane, produced by NOF Corporation under the trade name Perhexa 3M-40.³⁾Zinc white-containing sulfur, produced by Isurumi Chemical Industry Co., Ltd.⁴⁾Nocrack NS-6, produced by Ouchi Shinko Chemical Industrial Co., Ltd.⁵⁾Deformation under loading from an initial load of 98 N to a final load of 1,275 N

TABLE 4

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Flight ¹⁾	Carry (m)	233.0	232.2	231.1	233.2	232.1	232.5	231.8	229.5
	Total distance (m)	241.2	243.8	244.9	238.5	239.9	245.5	238.3	241.1
	Spin (rpm)	2805	2745	2700	2910	2855	2550	2952	2847
	Rating	good	good	good	poor	poor	good	poor	fair
Approach ²⁾	Spin (rpm)	5833	5821	5811	5849	5830	4100	5870	5832
	Rating	good	good	good	good	good	poor	good	good
Feel ³⁾	When hit with driver	good	good	good	good	good	good	good	poor
	When hit with putter	good	good	good	good	good	poor	good	good

¹⁾Flight was rated as follows, based on distance measured when ball was hit at a head speed of

50 m/s by a driver mounted on a swing robot

Good: Total distance at least 241 m

Fair: Total distance at least 241 m, but carry less than 230 m

Poor: Total distance 240 m or less

²⁾Approach was rated as follows, based on spin rate measured when ball was hit at a head speed

of 19 m/s by a sand wedge mounted on a swing robot

Good: Good spin (at least 5,500 rpm)

Poor: Inadequate spin (less than 4,500 rpm)

³⁾Average sensory evaluations for five professional golfers:

Good: Feel was appropriate and good.

Poor: Feel was too hard or too soft

As is apparent from the results in Table 4, the golf balls according to the invention all showed a good balance of distance, controllability on approach shots, and feel.

By contrast, the golf balls produced in the comparative examples each had drawbacks. In Comparative Examples 1 and 2, the hardness difference between the surface and center of the core was less than 18, resulting in much spin and a poor distance when the ball was hit with a driver. In Comparative Example 3, the cover was harder than the intermediate layer, and had an excessively high hardness. As a result, the amount of spin on approach shots was low and controllability was poor. In addition, the feel when hit with a putter was poor. The golf balls produced in Comparative Example 4 were two-piece balls which lacked between the cover and the core an intermediate layer of greater hardness than the cover. These balls had a lot of spin when hit with a driver, and thus a poor distance. In the golf balls produced in Comparative Example 5, the core hardness was lowered to reduce the high spin rate on impact with a driver in Comparative Example 4, but the resulting feel on impact with a driver was too soft.

Japanese Patent Application No. 2000-190640 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1 A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein said intermediate layer is composed of a resin material which is harder than the cover and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and said elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

2 The golf ball of claim 1, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90.

3 The golf ball of claim 1, wherein said core undergoes a deformation of 3.0 to 5.0 mm when the load applied

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thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

4. The golf ball of claim 1, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units

5 The golf ball of claim 1, wherein the intermediate layer has a Shore D hardness of 50 to 67.

6. The golf ball of claim 1, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units

7. The golf ball of claim 1, wherein the cover has a Shore D hardness of 45 to 60

8 The golf ball of claim 1, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover.

9. The golf ball of claim 1, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

10 The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

11 The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol

12 The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber

13 A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover, and has a greater hardness than the surface of the elastic core when compared using the same JIS-C hardness scale, and

said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface

14 The golf ball of claim 13, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90

15. The golf ball of claim 13, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units

16 The golf ball of claim 13, wherein the intermediate layer has a Shore D hardness of 50 to 67.

17 The golf ball of claim 12, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units

10

18 The golf ball of claim 12, wherein the cover has a Shore D hardness of 45 to 60.

19 The golf ball of claim 12, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover

20 The golf ball of claim 12, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

21 The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof

22 The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentafluorothiophenol

23 The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

24 A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover having a Shore D hardness of 45 to 58 and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and

said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface

25 The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof

26 The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol

27 The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber

* * * * *

EXHIBIT D

IN UNITED STATES DISTRICT COURT
DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD.,
and BRIDGESTONE GOLF, INC.,

Plaintiffs,

v.

ACUSHNET COMPANY,

Defendant.

C.A. No. 05-132(JJF)

DEMAND FOR JURY TRIAL

**PLAINTIFFS' RESPONSES TO DEFENDANT'S SECOND SET OF
INTERROGATORIES**

Pursuant to Rule 33 of the Federal Rules at Civil Procedure, Plaintiffs Bridgestone Sports Co., Ltd. and Bridgestone Golf, Inc. (individually or collectively "Bridgestone") hereby respond to Defendant's Second Set of Interrogatories Directed to Plaintiff dated December 13, 2005.

GENERAL OBJECTIONS

The General and Specific Objections set forth in Plaintiffs' First Responses to Defendant's First Set of Interrogatories are incorporated herein by reference.

In addition, Bridgestone objects to the definition of "Nike" as being overly broad, unduly burdensome and oppressive, on the grounds that it includes undefined entities, such as any parent, subsidiary, partner (including general and limited partners), member and/or affiliated entities, past or present. Bridgestone further objects on the grounds that this definition refers to third parties to this action that are unknown to Bridgestone.

Subject to, and without waiving, any of the General and Specific Objections, Bridgestone hereby responds to Interrogatory Nos. 25-38 as follows.

SPECIFIC OBJECTIONS AND RESPONSES

INTERROGATORY NO. 25

Identify each document produced by Bridgestone in response to any request in Defendant's First Set of Requests for the Production of Documents and Things (served on June 10, 2005) and Defendant's Second Set of Requests for the Production of Documents and Things (served on August 2, 2005) related to the use of organosulfur compounds in golf balls in any amount, including but not limited to the following sulfur-containing compounds: pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2-benzamidothiophenol, thiobenzoic acid, and zinc salts thereof.

RESPONSE TO INTERROGATORY NO. 25

In addition to the General Objections, Bridgestone objects to the interrogatory as being overly broad, oppressive, and specifically calling for information covered by the attorney work product doctrine. Bridgestone further objects to the interrogatory because Acushnet did not propound a specific Document Request for the information requested in the interrogatory. To the extent Bridgestone has produced documents related to the use of organosulfur compounds, Bridgestone further objects to the interrogatory as being unduly burdensome because Acushnet can ascertain an answer as readily as Bridgestone. Therefore, Bridgestone will not respond to the interrogatory.

INTERROGATORY NO. 26

For each Document produced by Bridgestone, identify each document produced by Bridgestone in response to any request in Defendant's First Set of Requests for the Production of Documents and Things (served on June 10, 2005) and Defendant's Second Set of Requests for the Production of Documents and Things (served on August 2, 2005), identify the source of the files for each such Document by identifying the name of the person from whose files such Document was located and the physical location in which such Document was located, including file numbers, room numbers, and building numbers and physical addresses.

RESPONSE TO INTERROGATORY NO. 26

In addition to the General Objections, Bridgestone objects to the interrogatory as being overly broad, unduly burdensome and oppressive. Bridgestone further objects to the interrogatory as being vague with respect to the terms "file numbers" and "building numbers".

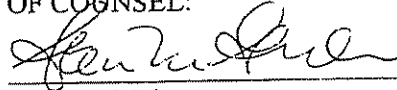
As to objections:

MORRIS, NICHOLS, ARSHT & TUNNELL

DATED: January 17, 2006

Jack B. Blumenfeld (#1014)
Maryellen Noreika (#3208)
Leslie A. Polizoti (#4299)
1201 N. Market Street
P.O. Box 1347
Wilmington, DE 19801
(302) 658-9200
*Attorneys for Bridgestone Sports Co., Ltd. and
Bridgestone Golf, Inc.*

OF COUNSEL:



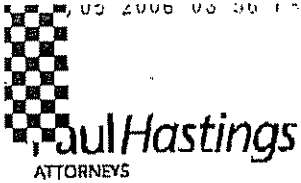
Robert M. Masters
John T. Callahan
Steven M. Gruskin
Raja Saliba
SUGHRUE MION, PLLC
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037
(202) 293-7060

VERIFICATION

I hereby declare under penalty of perjury under the laws of the United States that the facts set forth in the foregoing **PLAINTIFF'S RESPONSES TO DEFENDANT'S SECOND SET OF INTERROGATORIES** are true and correct to the best of my present knowledge and beliefs, although the truth of the entirety of each said response may not be known to me personally because said responses are based in part upon information received from others, and that I am authorized to execute this Verification on behalf of Plaintiff Bridgestone Sports Co., Ltd and Bridgestone Golf, Inc.

Dated: , 2006

EXHIBIT E



Paul, Hastings, Janofsky & Walker LLP
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FACSIMILE TRANSMISSION

to:	company/office:	facsimile:	telephone:
Brian S. Seal, Esq.	Howrey LLP	202-383-6610	
from:	facsimile:	telephone:	initials:
John K. Shin	(202) 551-1705	(202) 551-1825	JKS3
client name:		client matter number:	70416.00002
date:	May 5, 2006	pages (with cover):	3

comments:

If you do not receive all pages, please call immediately Facsimile Center: (202) 551-1275

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PaulHastings
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johnshin@paulhastings.com

May 5, 2006

70416.00002

VIA FACSIMILE TO (202) 383-6610

Brian S. Seal
Howrey LLP
1299 Pennsylvania Ave., N.W.
Washington, DC 20004

Re: Bridgestone Sports v. Acushnet
Your April 24, 2006 Letter Regarding JP 02-092378 Publication

Dear Brian:

This letter is in response to your letter of April 24, 2006 regarding Japanese Patent Publication No. 02-092378.

Despite your repeated assertions, Bridgestone is still not withholding any additional relevant documents relating to JP '378 publication. We previously produced file histories for JP '378 publication. After conducting another search including the files of Mr. Yoshihiko Fujii in response to your letter, we confirm that no other responsive documents exist in Bridgestone's possession.

In your letter, you further assert that even if JP '378 publication is not prior art under 35 U.S.C. §102(a), that it is relevant to derivation under 35 U.S.C. §102(f). Although we do not agree with your assertion, in any case, as we previously stated, no responsive documents exist in Bridgestone's possession other than the file histories which we have already provided to you.

Further, no counterpart applications to the Japanese patent application corresponding to JP '378 publication were filed in any other country.

Accordingly, Bridgestone believes it has produced all responsive documents.

We maintain that the Japanese application to Mr. Fujii is not prior art, and we will produce a certified English translation in due course.

05/05/2006 03:51 PM 202 551 1100

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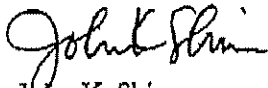
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Page 2

Regarding any responsive documents related to the use of organosulfur compounds in golf balls, we are still investigating and will provide Acushnet with an update in due course.

Sincerely,



John K. Shin
for PAUL, HASTINGS, JANOFSKY & WALKER LLP

EXHIBIT F

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robmasters@paulhastings.com

May 17, 2006

70416.00002

BY HAND DELIVERY

Alan M. Grimaldi
Howrey LLP
1299 Pennsylvania Ave., N.W.
Washington, DC 20004

Re: *Bridgestone v. Acushnet*

Dear Alan:

This letter responds to your May 5, 2006 letter laying out alleged deficiencies in Bridgestone's discovery responses.

I. ALLEGED DEFICIENCIES IN BRIDGESTONE'S DOCUMENT PRODUCTION

A. Development Documents for Golf Balls Practicing the Bridgestone Patents

Bridgestone has produced all documents relevant to Acushnet's Requests for Production Nos. 4 and 5 and believes that it has fully complied with these requests. Bridgestone asserts that any documents related to the commercial embodiments of its patents after the date of issue are irrelevant and non-responsive. As such, Bridgestone will not supplement its production at this time. To the extent Acushnet disagrees, please explain the relevance of this information. Furthermore, please explain why Acushnet has not produced the same kind of information.

As for Interrogatory No. 12, Bridgestone is satisfied with the completeness of its response on this matter and believes it has fully responded to this Interrogatory. As such, Bridgestone will not supplement its response to this interrogatory at this time. To the extent Acushnet maintains that golf balls made and sold only in countries outside of the U.S. should be identified in response to Interrogatory No. 12, which pertains solely to U.S. patents, explain your reasoning and support for such a position. Also, explain the relevance of such information to the issues in this case.

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ATTORNEYS

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May 17, 2006

Page 2

B. Documents Relating to the Testing of Third Party Golf Balls

Bridgestone has produced all non-privileged, non-work product documents related to the testing of balls relied on by Acushnet prior to the May 1, 2006 supplementation date. Further, Bridgestone responded to the November 10, 2005 letter on December 22, 2005. (See Letter from Gruskin to Moore re Bridgestone's Response to Acushnet's Alleged Deficiencies in Bridgestone's Document Production.) Accordingly, there is no need for Bridgestone to supplement its production.

Bridgestone will provide an inventory of balls shortly.

C. Documents Relating to the Callaway Litigation

Bridgestone has previously produced a large number of documents relating to both the Callaway litigation (see BSP099230-629) and the licensing agreement with Callaway (see BSP058856-908). No other non-privileged documents exist. Bridgestone has searched its records and does not have a copy of the Cadorniga declaration.

D. Manufacturing Guidelines for Bridgestone Prior Art Golf Balls

Bridgestone responded to your April 6, 2006 letter on this issue on April 19, 2006. (See Letter from White to Seal re Alleged Deficiencies in Bridgestone's Discovery Response, April 19, 2006). Bridgestone stands by its assertions in that correspondence. I am enclosing a courtesy copy for your review.

E. Samples of Bridgestone's Retail Packaging

On November 18, 2005, a mere 8 days after your letter to us on this issue, Bridgestone produced copies of retail packaging for the accused products (See, e.g., BSP094584-600). You may inspect the originals in our office, but otherwise our response is complete.

F. Documents Relating to Testing Protocols

Bridgestone responded to your April 6, 2006 letter on this issue on April 19, 2006. (See Letter from White to Seal re Alleged Deficiencies in Bridgestone's Discovery Response, April 19, 2006). Bridgestone stands on its position in that correspondence.

Regarding the issues raised in your April 18, 2006 letter regarding the equipment for measuring 300% modulus, Bridgestone believes it has produced all relevant non-privileged documents at this time.¹ (See, e.g., documents BSP034053-403 and BSP034735-BSP035050).

¹ In a separate letter, Bridgestone has requested the return of the documents referenced by you, BSP167255-59, as part of a range of privileged documents inadvertently produced

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Page 3

Additionally, further to your letter of April 21, 2006, Bridgestone is producing BSP202133-207, which are unrevised testing protocols. Although the previously produced COR testing protocol states that it was revised in August, 2002, the document was in fact created on that date.

Finally, as for designating certain Bridgestone test protocols "highly confidential," Bridgestone maintains that these documents are properly designated under the Protective Order.

G. Documents Regarding the Testing of Pro V1's Cover Thickness

Bridgestone responded to your April 6, 2006 letter on the issue of cover thickness measurements on April 19, 2006. (See enclosed Letter from White to Seal re Alleged Deficiencies in Bridgestone's Discovery Response, April 19, 2006). Bridgestone stands on its positions in that correspondence.

H. Documents Related to the Testing of Materials for 300% Modulus

Regarding the issues raised in your April 6, 2006 and April 18, 2006 letters regarding the testing of materials for 300% modulus, Bridgestone believes it has produced all relevant non-privileged documents at this time. Contrary to your assumptions, Bridgestone does not routinely perform competitive testing of golf balls for 300% modulus.

I. Documents Regarding Bridgestone's Strategy Office

The document referred to herein, BSP172625, does not, as you allege, indicate that Bridgestone has a Strategy Office. Rather, it suggests the idea of having a Strategy Office. Thus, there is not now nor has there ever been a Strategy Office at Bridgestone and therefore no documents responsive to this request exist.

J. The "Summary Pro V1 Spreadsheet"

Bridgestone is producing BSP202204-286, which is the spreadsheet attachment to BSP145526, with this letter.

K. Golf ball Development Reports

Bridgestone is producing BSP202097-132, which are the remaining golf ball development reports. As these meetings were not held every month, there are many months for which no development report exists. Additionally, please note that the document for the January 2002 meeting is mistakenly labeled "January 8, 2001."

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Page 4

L. Bridgestone Prior Art and Acushnet's Invalidity Contentions

It is Bridgestone's belief that the documents requested in Acushnet's April 21, 2006 letter are both irrelevant and non-responsive. Furthermore, as all of the patents you referenced have issued from the U.S. Patent Office, you are able to obtain copies of the file histories. As such, Bridgestone will not be supplementing its production.

Bridgestone is not withholding documents related to the development of the patents in suit. The fact that Bridgestone filed other patents related to golf balls or that the inventors of the patents in suit are named inventors on other patents does not mean that other responsive, relevant documents exist. Acushnet is simply looking for an excuse to stall this case out as long as possible by raising alleged deficiencies in Bridgestone's production.

M. Documents Related to the "New" Nike Golf Balls

We certainly look forward to discussing the "new" Nike golf balls with you at our meet and confer next week. However, we believe that Acushnet needs to explain the basis for its new allegations of infringement before we consider the request.

N. Missing Pages in Documents

Documents BSP088712-785 and BSP088811-25 were produced in the manner in which they were kept. Bridgestone produced all pages of these documents that were in their files. Document BSP109522 appears to have 18 pages, but this is simply due to a formatting issue. When printed out, the last 2 pages are blank, and thus were not produced. As for the remainder of its production, Bridgestone is satisfied with its completeness.

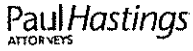
II. ALLEGED DEFICIENCIES IN BRIDGESTONE'S INTERROGATORY RESPONSES

A. Employee Numbers for Bridgestone Employees

Bridgestone responded to your April 6, 2006 letter on this issue on April 19, 2006. (See enclosed Letter from White to Seal re Alleged Deficiencies in Bridgestone's Discovery Response, April 19, 2006). Bridgestone stands by its assertions in that correspondence.

B. Bridgestone Golf Balls Practicing the Patents-in-suit

Bridgestone contends that it has fully complied with the Court's November 2, 2005 order in regard to Interrogatory No. 9 by incorporating the response of Interrogatory No. 12 identifying the Bridgestone golf balls and Callaway golf balls. Furthermore, the interrogatory is limited by geography because it refers to only to U.S. patents. As to



Alan M. Grimaldi
May 17, 2006
Page 5

the Nike golf balls, Bridgestone does not in the course of its business make a determination as to which balls, if any, are covered by any Bridgestone patents and the Court was clear that Bridgestone did not have to conduct such an analysis. As such, there is no need for Bridgestone to supplement its response to this interrogatory.

C. Licenses to the Patents-in-suit

Bridgestone's response to Interrogatory No. 11 is complete.

D. Documents Relating to Organosulfur Compounds in Golf Balls

Bridgestone's response to Interrogatory No. 25 is complete and Bridgestone stands on its objections.

E. Documents Relating to the Bridgestone Patents-in-suit

Bridgestone's responses to Interrogatories Nos. 29-38 is complete, and Bridgestone stands on its objections. As such, Bridgestone will not supplement its response to these interrogatories at this time.

F. Individuals Named on Bridgestone's Privilege Log

Each of the names listed by you in your April 18, 2006 letter identified as not being listed in Bridgestone's response to Acushnet's Interrogatory No. 39 is the result of a typographical error in the privilege log, and thus a supplementation of Interrogatory No. 39 will not be necessary.

1. Shinodo – Should be Shindo, J.
2. Ishikawa, Y. – Should be Ishikawa, T.
3. Sato – Should be Sano, M.
4. Ichinose, T. – Should be Ichinose, J.
5. Kitama, K. – Should be Kitamura, K.
6. Na – Should be Nanba, A.
7. Surdiffe, N. – Should be Sutcliff, N.



Alan M. Grimaldi
May 17, 2006
Page 6

G. Bridgestone's Response to Acushnet's Interrogatory No. 6

Bridgestone has provided a complete response to this interrogatory. Acushnet is seeking information that is neither relevant to this case nor reasonably calculated to lead to the discovery of admissible evidence with this interrogatory. Please explain the basis for believe that the date of conception, if earlier than the filing date of the Japanese applications and/or is not being relied upon by Bridgestone, is relevant. As such, Bridgestone will not supplement its response to this interrogatory at this time.

H. Individuals Most Knowledgeable About Testing Acushnet Products

Bridgestone will supplement its response to Interrogatory 14 to identify persons knowledgeable about testing.

I. Bridgestone's Response to Acushnet's Interrogatory No. 15

Bridgestone confirms it is seeking a reasonable royalty and not lost profits.

J. Doctrine of Equivalents and Prosecution History Estoppel

Any discussion regarding the interpretation of claim terms is premature at this point in the proceedings. Bridgestone will follow the Court's schedule in preparation for the *Markman* hearing.

K. Bridgestone's Response to Acushnet's Interrogatory No. 27

Bridgestone is satisfied with the completeness of its response to this interrogatory and believes it has fully complied with this request. As such, Bridgestone does not believe it needs to supplement this response to this interrogatory but we will review the documents you have identified to confirm.

PaulHastings
ATTORNEYS

Alan M. Grimaldi
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Page 7

**III. ALLEGED DEFICIENCIES IN BRIDGESTONE'S ANSWERS TO
ACUSHNET'S REQUESTS FOR ADMISSIONS**

Bridgestone is satisfied with the completeness of its responses to Acushnet's Requests for Admission Nos. 12-20 and stands by its objections. As such, Bridgestone will not supplement its responses to these Requests for Admission at this time.

We look forward to discussing these issues with you during the meet and confer scheduled for May 22.

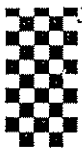
Sincerely,

A handwritten signature in black ink, appearing to read "Robert M. Masters", followed by a stylized flourish or second signature.

Robert M. Masters
of PAUL, HASTINGS, JANOFSKY & WALKER LLP

LEGAL_US_E # 70859872 3

EXHIBIT G



200 Pennsylvania Avenue, NW
Washington, DC 20037-3213

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F 202.293.7860

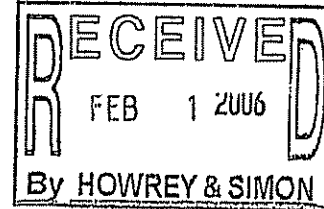
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FAX

Date Brian S. Seal
Of Howrey LLP
Fax 202-383-6610
From Steven M. Gruskin
Subject Bridgestone v. Acushnet
Our Ref L10518 Your Ref
Pages 3
(Including cover sheet)



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Steven M. Gruskin
T (202) 663-7372
sgruskin@sughrue.com

January 31, 2006

Via Facsimile: (202) 383-6610

Mr. Brian S. Seal
HOWREY LLP
1299 Pennsylvania Ave., N.W.
Washington, D.C. 20004

Re: Bridgestone Sports v. Acushnet
Our Ref.: L10518
Your Letter of January 20, 2006

Dear Brian:

In response to your letter dated January 20, 2006, we have the following comments:

1. Interrogatory No. 25

Bridgestone's objection is not made pursuant to Rule 33(d), but rather based on burden. Acushnet can just as easily review the documents as Bridgestone to determine which documents relate to the use of organosulfur compounds. Bridgestone should not be required to do Acushnet's job.

2. Interrogatory No. 28

Again, Bridgestone's objection is not made pursuant to Rule 33(d). In any event, Bridgestone identified the relevant documents in its response. The fact that these documents are in Japanese is of no consequence. Moreover, in a previous meet and confer, you indicated to us that Acushnet had obtained full English language translations of the documents produced by Bridgestone. It is not clear then why you now contend that it is unduly burdensome to translate these documents.

3. Interrogatory Nos. 29-38

Once again, Bridgestone is not relying on Rule 33(d), and consequently there is no need to "identify the bates numbers for each document from which the answers may be derived."

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Mr. Matthew J. Moore
HOWREY LLP
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Acushnet can review Bridgestone's production and make its own determination as to what documents either relate to or do not relate to the subject matter of the request. Moreover, Bridgestone stands on its objection that the request is premature, since it calls for a legal conclusion. Finally, you indicate that Bridgestone's identification of documents it believes relate to the subject matter of the request is "relevant to questions of claim construction, infringement (both literal and under the doctrine of equivalents), and invalidity." However, you provide no explanation of why that is so. Please therefore let us know the basis for this assertion.

4. RFA Nos. 1-3

Bridgestone stands on its response to these requests for admission. Bridgestone has admitted that the statements appear in its Opposition paper, and no further response is deemed necessary.

5. RFA No. 5

Again, Bridgestone stands on its response to this request for admission as written.

6. RFA Nos. 12-20

Bridgestone is not required to correct Acushnet's definition of "prior art", nor will it attempt to do so. Moreover, there is no contradiction between Bridgestone's response to Acushnet Interrogatory No. 8 and its response to these requests for admission. Bridgestone has not admitted that the "art that Acushnet has identified to Bridgestone" is "prior art" as defined in Acushnet's requests for admission.

7. RFA Nos. 21-22

Bridgestone stands on its response to these requests as presently worded.

We are available for a meet and confer to discuss any issues raised herein or in our other correspondence.

Very truly yours,

Steven M. Gruskin

SMG